Quarterly Progress Report

For Period

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# FUNDAMENTAL STUDIES OF THE METALLURGICAL, ELECTRICAL, AND OPTICAL PROPERTIES OF GALLIUM PHOSPHIDE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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CLEVELAND, OHIO

Work Performed By

Solid-State Electronics Laboratories
Stanford University
Stanford, California

PROJECT 5112: THE PROPERTIES OF RECTIFYING JUNCTIONS IN $GaAs_xP_{1-x}$

National Aeronautics and Space Administration
Grant NsG-555
Project Leader: G. L. Pearson
Staff: S. F. Nygren*

The purpose of this project is to study the preparation and characterization of rectifying junctions in GaP and $GaAs_xP_{1-x}$. In particular, we wish to relate the structure of the crystals to the electrical properties of the junctions. During this quarter we have developed improved techniques for growing GaP single crystals by either the vapor epitaxial or the liquid epitaxial methods. We have also studied zinc diffusion in GaP as a function of preannealing time.

A. Crystal Growth by Vapor Epitaxy

In general, it is desirable for semiconductor crystals to be as free from imperfections as possible. With this viewpoint in mind, we have attempted to reduce the number of stacking faults that are grown into our crystals. The following improved seed handling procedures have been incorporated into our growth technique:

1. After the saw damage is lapped off the seed crystal, it is etched for 2.5 minutes in 9 $HNO_3$:1 HF (instead of the one minute used previously).

2. The gallium source is presaturated with phosphorus while the seed is in the standby position. This is meant to minimize the amount of free gallium that might be transported to the seed.

3. The seed is vapor etched in its growth position in the reaction tube just before deposition of GaP is begun. This is accomplished by raising the seed temperature to 930°C for ten minutes while the usual

*NSF Fellow

proportions of $H_2$ and $PCl_3$ vapor are flowing through the reaction tube.

Gallium phosphide crystals grown without the improved seed handling technique typically have dislocation densities of $\epsilon_1 = 1 \times 10^6$ $cm^{-2}$ and stacking fault densities of $\epsilon_2 = 700$ $cm^{-1}$. The first crystal grown with the improved technique had $\epsilon_1 = 1 \times 10^6$ $cm^{-2}$, $\epsilon_2 = 35$ $cm^{-1}$, averaged over several square millimeters of area.

B. Crystal Growth by Liquid Epitaxy

Our current objective with the GaP liquid epitaxial system is to grow planar p-n junctions with controlled doping levels in the n- and p-type regions in hopes of making superior diodes. Junctions that are extremely planar over distances greater than 500 μ were formed by observing the following precautions:

1. The growth surface [{111}P] of the seed was mechanically polished in Linde A lapping compound. In some cases it was also etched in 2 $HNO_3$:1 HCl. This etchant removes about 2.3 μ/min from the {111}Ga and {111}P faces combined. It must be strongly agitated to prevent pits from forming on the {111}P face.

2. An argon atmosphere was used. Actually, using an evacuated ampoule instead of a reaction tube preserves the seed surface even better, but using an ampoule large enough to contain the graphite boat is inconvenient. A low maximum temperature is also found to be desirable, and 1050°C was chosen as an acceptable compromise between minimum seed erosion and maximum GaP solubility in the Ga solution. Table 1 summarizes the seed erosion under various conditions.

3. Meltback of the seed is minimized by not pouring the gallium solution over the seed until they have started to cool.

Figure 1 shows a cross section of an n-type GaP crystal with a p-type liquid epitaxial layer. The layer was grown on a (nominally) undoped n-type seed, previously grown by vapor epitaxy, observing the above precautions, and using a solution containing a 5.0g gallium, 0.35g GaP, and 4.0 mg zinc. The acceptor concentration at the surface of the layer is $5 \times 10^{17}$ $cm^{-3}$. Since the segregation coefficient of zinc in GaP varies with temperature, the doping level in the layer is not uniform. It is higher near the interface than at the surface. Diodes were made from this crystal and were seen to exhibit green electroluminescence.

The cross section shown in Fig. 1 has been etched to show crystal imperfections and the p-n junction. It is seen that the melt grown layer is much more perfect than the seed and that the junction is quite planar.

C. Zinc Diffusion in GaP

To determine the effect of preannealing on zinc diffusion in GaP several samples from the same GaP crystal were annealed in vacuum for various times at 795°C. Then they were quenched and sealed into an evacuated diffusion ampoules with elemental zinc. They were diffused for 1.5 hours at 795°C.

It was found that annealing in vacuum for times up to at least 21 hours changed the crystal defect structure little if at all. The pre-annealing does change the zinc diffusion, however. See Fig. 2. In the unannealed sample, the maximum depth of the diffusion spikes is about

4 times as much as the diffusion depth in the more perfect parts of the crystal. In the annealed samples, the ratio drops to 3. This is an improvement, but it still leaves a very irregular diffusion front.

TABLE 1

Surface Erosion of Liquid Epitaxial Seeds and Various Conditions*

| Gas | Flow | Maximum Temperature | Initial Seed | Mass Loss | Initial Seed Thickness | Thickness Loss |
|---|---|---|---|---|---|---|
| Purified $H_2$ | 150 $cm^3$/min | 1140°C | 30.55 mg | 11.36 mg | 316 μ | 101 μ |
| Purified $H_2$ | 150 $cm^3$/min | 1050°C | 14.12 mg | 1.00 mg | 169 μ | 11.9 μ |
| Purified $H_2$ | 20 $cm^3$/min | 1140°C | 9.30 mg | 7.65 mg | 204 μ | 168 μ |
| Generated $H_2$ | 20 $cm^3$/min | 1140°C | 10.75 mg | 6.90 mg | 184 μ | 118 μ |
| Vacuum, $2X10^{-4}$ torr Ampoule, 48 $cm^{-3}$ | 0 | 1140°C | 11.20 mg | 1.17 mg | 168 μ | 17.6 μ |
| Vacuum | Diffusion Pump Continuously Pumping on Reaction Tube | 1074°C | 11 mg | 11 mg | 180 μ | 180 μ |
| Argon | 20 $cm^3$/min | 1140°C | 15.21 mg | 2.01 mg | 205 μ | 27 μ |

*Seed is placed in graphite boat without any gallium solution. It is then heated from room temperature to the maximum temperature in the experimental atmosphere. Finally it is cooled quickly (remaining in the experimental atmosphere) and observed.

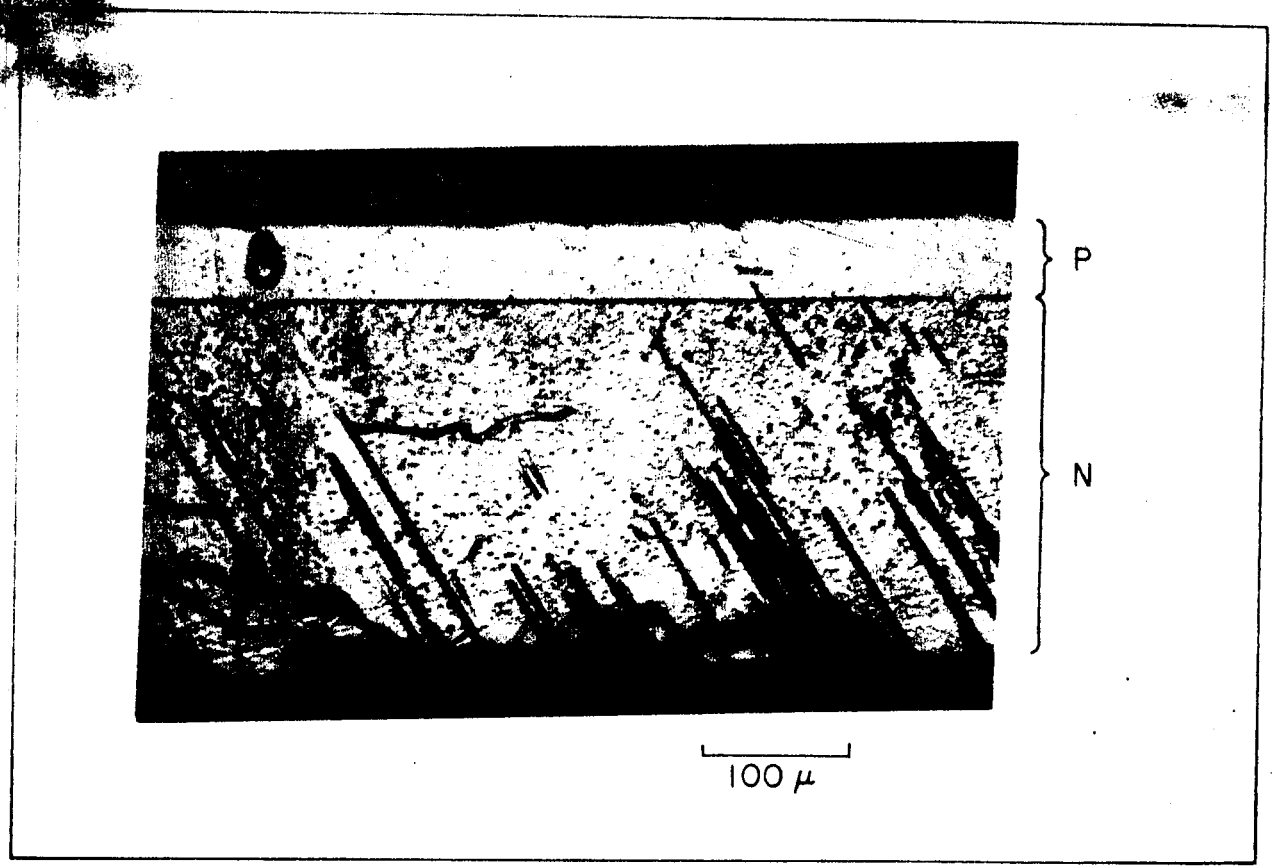


FIG. 1 - A {111} cross section of a p-type liquid epitaxial layer on an n-type GaP substrate. The surface has been etched to show the p-n junction and the crystal imperfections.

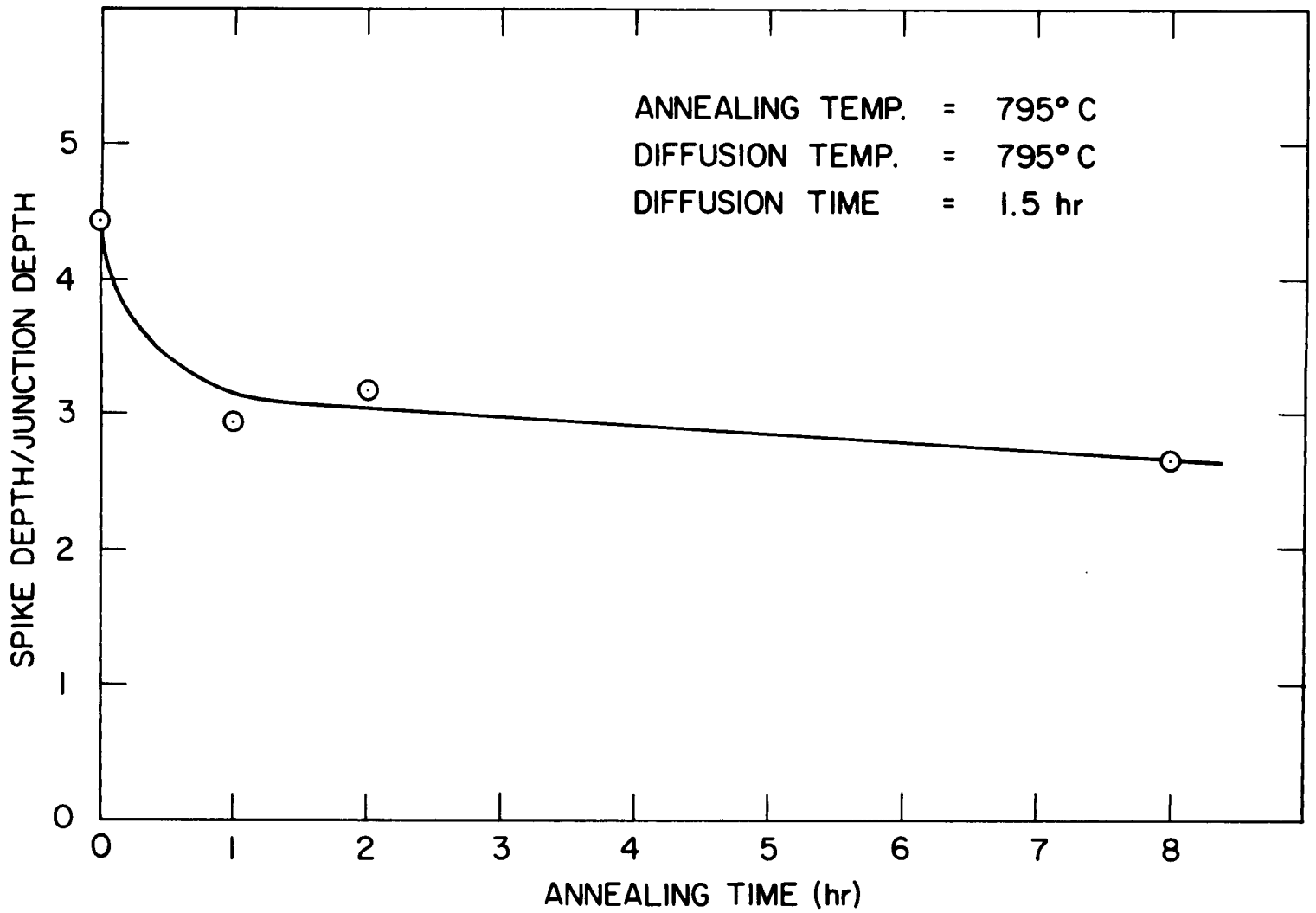


FIG. 2 - Zinc diffusion spike depth in GaP compared to normal diffusion depth as a function of preannealing time.

PROJECT 5115: SEMICONDUCTOR DEVICES FOR HIGH TEMPERATURE USE

National Aeronautics and Space Administration
Grant NsG-555
Project Leader: G. L. Pearson
Staff: Y. Nannichi

The purpose of this project is to prepare power rectifiers and solar batteries which will operate at temperatures up to 500°C.

Power Rectifier

A GaP Schottky barrier diode (Fig. 1) is planned for the power rectifier. There are several problems which must be solved before a completed device can be prepared. These include:

(1) preparation of an n-type single crystal of GaP of good quality, both electrically and crystallographically,

(2) making good ohmic contact to the n-type GaP crystal,

(3) obtaining a clean surface for the Schottky barrier and

(4) evaporating a suitable metal on the crystal in order to get a good Schottky barrier.

Solar Battery

Figure 2 shows a heterojunction of GaAs and GaP which we propose for the solar battery. Though it has been known that this structure will provide a wider range of spectral response and possibly a higher efficiency, no one has yet been successful in preparing a good heterojunction for this purpose. It seems feasible to obtain such a junction using the epitaxial techniques developed in this laboratory.

Research Program

The research will be carried out in the following respects:

(1) N-type GaP crystals of about 100 μ thickness will be grown by means of both liquid and vapor epitaxial methods. The desirable resistivity range is 1-10 ohm-cm. The impurity distribution will be calculated from C-V characteristics.

(2) Ohmic contacts to the high resistivity n-type GaP crystal will be obtained either through a sulfur-diffused layer or through a hetero-$nn^+$-junction of GaP and GaAs. The study of diffusion of sulfur into GaP is being carried out by A. Young in this laboratory on NsG-155.

The hetero-$nn^+$-junction will consist of n-GaP, $n^+$-GaAs, and the transition region of $GaAs_xP_{1-x}$ in which both the composition ratio x and the impurity concentration vary gradually along the growth direction. To our knowledge, a heterojunction usually has in its transition region a barrier which is supposed to be due to the lattice misfit. This kind of barrier in the heterojunction structure is not desirable, so we will try to make a wide transition region by controlling the composition ratio during the vapor epitaxial growth. If we make a 5 μ thick transition region, the misfit in the lattice constants of GaP and GaAs is expected to take place in a thickness of about $10^4$ atomic layers.

A metal film will be deposited on the heavily doped layer which has been produced by sulfur diffusion or on the $n^{++}$ GaAs substrate to form an ohmic contact. A hetero-$nn^+$-junction without built-in barriers should provide a good contact especially in the forward direction. Needless to say, at elevated temperatures where GaAs is intrinsic or in the saturation range, GaAs will act as a conductor rather than a semiconductor and the good conducting channel will remain.

(3) It is extremely important to prepare a clean surface in order to obtain a reproducible Schottky barrier. A cleaved surface is certainly ideal but it is not practical. Low energy $A^+$ bombardment will produce a good surface.[1] Best conditions as to acceleration voltage, vapor pressure of argon, ion current density, annealing temperature, etc., will be studied for GaP. Argon atoms adsorbed on the GaP surface should be desorbed by successive electron bombardment. As the desorption energy is less than a few volts, only a very low energy electron beam is required.

(4) Chromium films will be evaporated in vacuum on GaP to form the Schottky barrier. If necessary, such metals as W, Mo, and Ta which should have high eutectic temperatures with GaP, will be evaporated by means of an electron gun.

(5) We will try to grow a hetero-pn-junction of GaP and GaAs in a manner similar to that mentioned in (2). $AsCl_3$ doped with n-type impurities and $PCl_3$ doped with p-type impurities will be kept in bubblers in the hydrogen line. At first, n-type GaAs will be grown on the n-type GaAs substrate. Then by gradually closing the valves of the $AsCl_3$ bubbler while opening those of the $PCl_3$ bubbler, the transition region will be grown until a p-type GaP layer is grown. Electrical, spectral and temperature characteristics will be studied. There may also be magnetic or polarization effects in the heterojunction.[2]

As this process requires heavily doped materials, a separate set up for the vapor epitaxy is being constructed.

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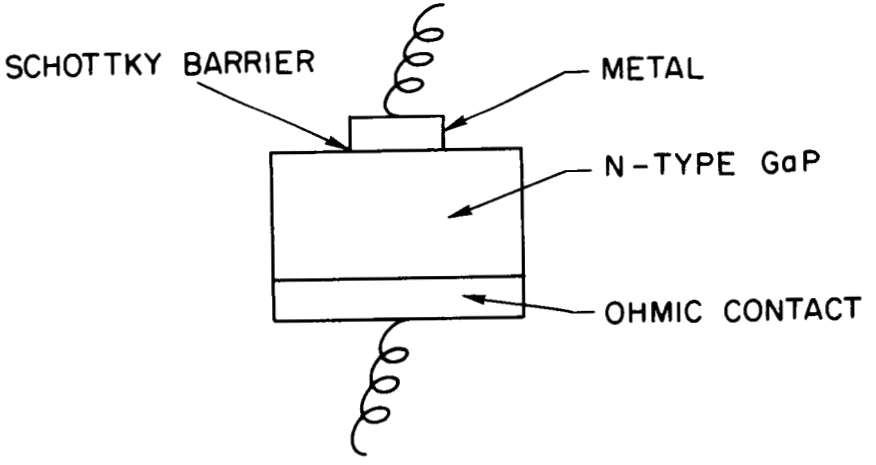


FIG. 1 - Structure of Schottky Barrier Diode.

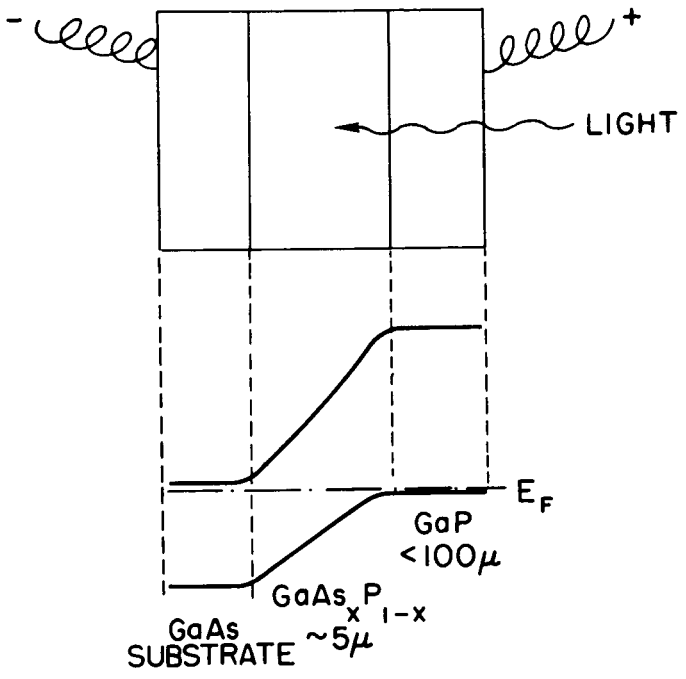


FIG. 2 - Structure and Band Diagram of a GaAs-GaP Heterojunction Solar Battery.

PROJECT 5116: DONOR IMPURITIES IN GaP

National Aeronautics and Space Administration
Grant NsG-555
Principal Investigator: G. L. Pearson
Staff: A. Young*

The purpose of this project is to study the behavior of shallow donors in gallium phosphide. In particular, S, Se, and Te will be diffused into GaP to determine solubility and diffusion parameters. This information will be useful in delineating the properties of GaP doped with these shallow donor impurities.

Doping Efficiency of Diffused Layer

We have not yet obtained incremental resistivity data on our diffused layers of sulfur in GaP. Measurements on one sample (C-3), however, show that the sheet resistivity decreased by a factor of 6 - 7 after diffusion. If we assume a uniform diffused layer of 10 $\mu$ depth (estimated from radiotracer data), then the average carrier concentration in the layer increased by a factor of 500 to $1.6 \times 10^{18}$ $cm^{-3}$. This is in the range of dopings obtained by other methods, e.g., vapor epitaxial and solution growth, for shallow donor impurities in GaP.

P-N Junctions

Efforts were made to detect possible non-planarity in the sulfur diffusion front by diffusing sulfur-35 into p-type GaP. The base material was grown by the vapor phase epitaxial technique and doped from a Zn-Ga alloy source. No junction was found when the crystal was angle-lapped and etched.

The possible explanation for this result confirms calculations made by Dierschke concerning the doping profile in the epitaxial material

*NSF Fellow

used.[1] Hall measurements showed that the B face was p-type with an apparent hole concentration 2-3 X $10^{16}$ $cm^{-3}$. The A face, however, was n-type with a carrier concentration in the $10^{14}$- $10^{15}$ $cm^{-3}$ range. Dierschke's calculations predict a zinc surface concentration of 1.5 X $10^{19}$, with concentration decreasing three orders of magnitude in 8 mils. Thus, the A face would be expected to be converted to n-type, or become highly compensated. The undiffused crystal was cleaved and etched, revealing a p-n junction approximately in the center of a 16 mil sample.

These results demonstrate the non-homogeneous doping obtained from crystals grown by the method discussed. We hope to obtain homogeneous p-type crystals by the same vapor epitaxial technique, but using a volatile organometallic compound - diethyl zinc - as the doping source.[2]

Oxide Masking

Silicon oxide ($SiO_2$) films approximately 5000Å thick were deposited on GaP crystals by oxidation of silane.[3] Diffusions of sulfur in the presence of excess phosphorus were performed at 1200°C for 12 hours. The oxide films were very adherent under these conditions, and good surfaces were retained. (In contrast, films 1000Å thick, obtained by electron bombardment of an $SiO_2$ source, tended to flake off under diffusion conditions.) Quantitative results are not available but preliminary experiments indicate that significant amounts of sulfur can be diffused through the films. Surface concentrations are lower than in the absence of the oxide films, but use of such films may be of practical importance in the actual fabrication of devices.

Diffusion Profiles

An etching technique has been used to check some of the

previously determined profiles. The etch is (8g $K_3(CN)_6$:12g KOH:100g $H_2O$)[4] which reveals dislocations and stacking faults on the A face and is a polishing etch on the B face. The results shown in Fig. 1 indicate that the profile is more complex than previously thought, and that the mechanical lapping technique used earlier gave only a gross approximation to the actual profile. A 3 μ layer of rapidly decreasing concentration is followed by a more nearly erfc variation. This profile is more nearly like those observed for sulfur, selenium, and tin in GaAs.[5,6]

In our radioactive counting measurements, absorption of the 0.167 MeV sulfur-35 beta particles has been taken into account.[7,8] Figure 2 shows a plot of the absorbing power of various materials as determined in this laboratory. We have assumed the absorption coefficient for the betas in GaP to be the same as that in aluminum.

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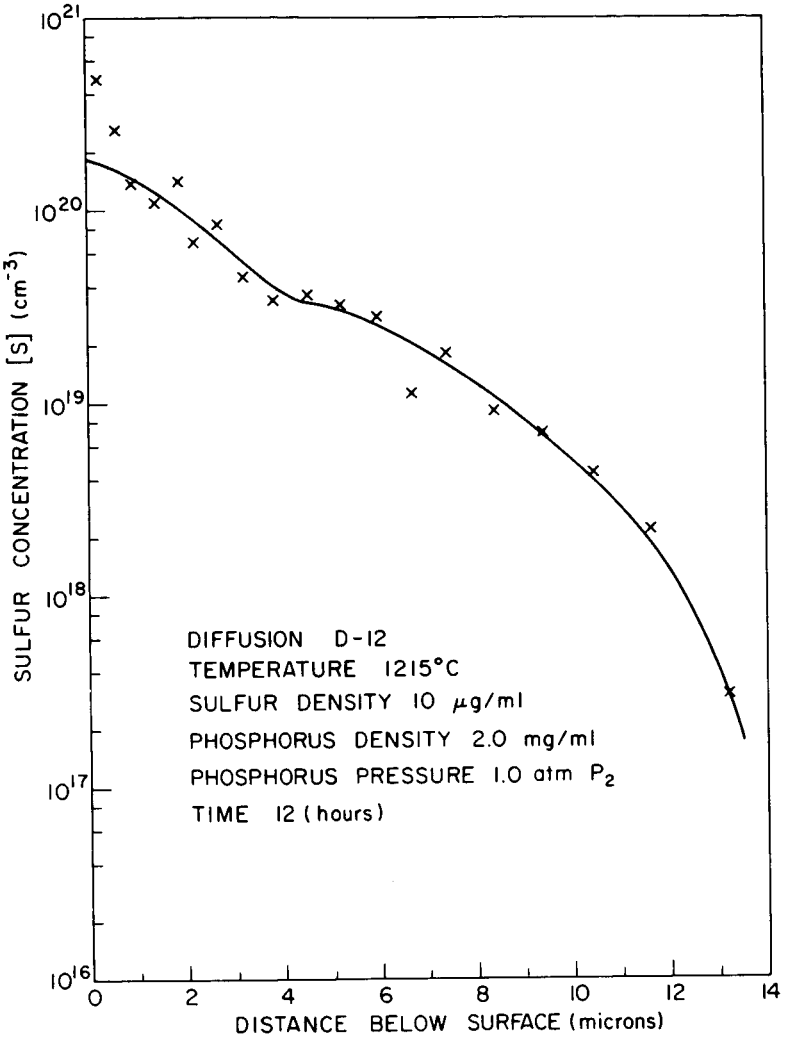


FIG. 1 - Diffusion Profile of Sulfur in GaP Obtained by An Etching Technique.

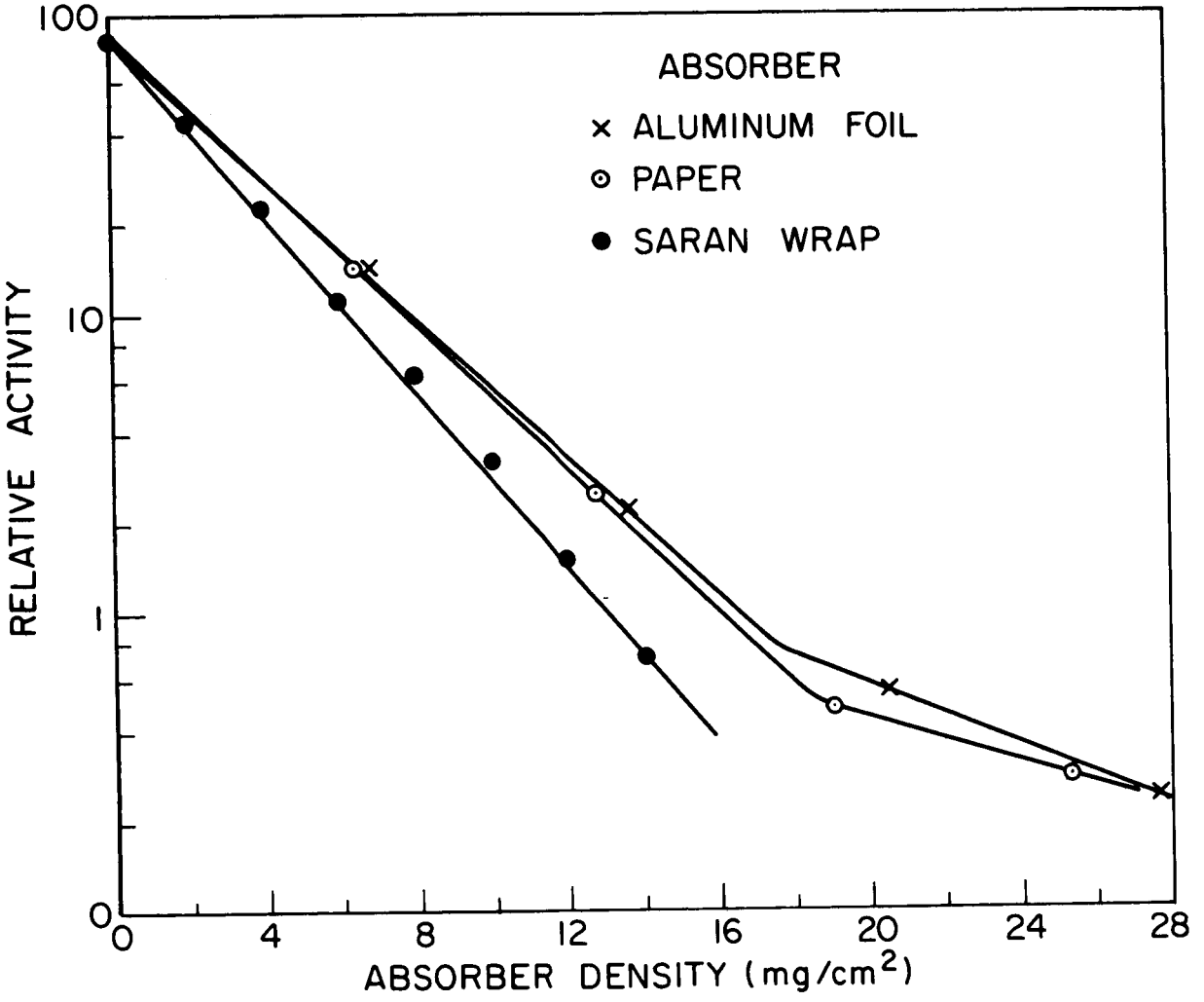


FIG. 2 - Absorption of Sulfur-35 Beta Particles in Various Materials.